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Wettability of R$(01\bar{1}2)$ single crystalline and polycrystalline α-Al_2O_3 substrates by Al–Si alloys over wide composition and temperature ranges

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Abstract The wetting behaviors of R$(01\bar{1}2)$ single crystalline and polycrystalline α-Al_2O_3 substrates by Al–Si alloys were studied over wide composition and temperature ranges. The wettability is quite good for all compositions of the alloys. The effect of temperature is moderate while that of the composition is significant. The dependence of the wettability on the alloy composition displays a ''valley'' profile with the minimum value appearing in the range of 60–70at.%Si. The wetting improvement by the addition of Al to Si mainly results from the decrease in the solid–liquid interfacial free energy by the Al segregation at the interface, while that by the addition of Si to Al results from the decrease in the surface tension of the liquid by the Si segregation.

Introduction

The wettability of ceramics by molten metals plays a key role in fabricating metal-ceramic composites. The wettability is usually characterized by the contact angle, θ, which is related to the surface free energies by Young's equation

$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \tag{1}$$

where σ_{sv}, σ_{sl} and σ_{lv} are the interfacial free energies of the solid–vapor, solid–liquid and liquid–vapor interfaces, respectively. Generally speaking, the condition $\theta < 90°$ indicates that a solid is wetted by a liquid, and $\theta > 90°$ indicates nonwetting, with the limits $\theta = 0°$ and $\theta = 180°$ defining complete wetting and complete nonwetting. A prerequisite for a liquid metal to spontaneously penetrate into a porous solid with cylindrical pores is $\theta < 90°$ [1].

The wettability of alumina by liquid Al [2–10] or Si [11–14] has been extensively investigated, however, little information is available concerning the wettability of alumina by Al–Si alloys [15], particularly with high Si concentrations. In a previous paper [16], we reported the wetting behavior of R$(01\bar{1}2)$-facet α-Al_2O_3 single crystals by Al–Si alloys at 1723 K. In this article, we present a more comprehensive study on the wetting behaviors of both the R$(01\bar{1}2)$-facet single crystalline and polycrystalline α-Al_2O_3 substrates by the Al–Si alloys over wide composition and temperature ranges.

Experimental procedure

Wetting experiments were performed using an improved sessile drop method described in detail elsewhere [10]. The substrates used were R$(01\bar{1}2)$-facet α-Al_2O_3 single crystal wafers with dimensions of ϕ 20 mm × 1 mm (produced by Kyocera Corp., Kyoto,

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Japan) and polycrystal plates with dimensions of 20 mm × 20 mm × 3 mm (produced by Kojundo Chemical Co., Ltd., Saitama, Japan). Both kinds of samples have a purity over 99.99 wt.%. The single crystal wafers were cut along their crystallographic plane, i.e., R$(01\bar{1}2)$, with an orientation error of ±0.3°, and one side of the surfaces was polished to an average roughness (R_a) value of 3 nm, as measured by a surface profilometer (Dektak 3, Veeco Instruments, Inc., NY, USA). The polycrystalline surfaces were mechanically ground on diamond discs and then polished by diamond pastes down to 0.25 μm to obtain an R_a value of less than 100 nm. The dropping materials were high purity Al (99.99 wt.%) and Si (99.9999999 wt.%) in the form of small segments. For only measuring the contact angle, the drop (Al and Si) weight was about 0.12–0.15 g. However, for simultaneous determining the surface tension, the drop weight was in the range of 0.25–0.30 g. The Al–Si alloys for any desired composition were made in situ during the experiments as briefly described in the following section.

The materials were first carefully ultrasonically cleaned in acetone and then the α-Al_2O_3 substrate was placed in a stainless-steel chamber in a horizontal position, while the Al and Si segments were placed in a glass tube located outside the chamber. The glass tube was connected to an alumina dropping tube (99.6 wt.% purity) with a small hole ($\phi = 1$ or 1.5 mm) in its bottom through which the samples could be dropped onto the substrate after they were melted. The chamber was heated in vacuum [$(1–5) \times 10^{-4}$ Pa] to the experimental temperature and then a purified Ar–3%H_2 gas with an oxygen partial pressure of the order of 10^{-18} Pa (measured by an oxygen sensor of ZrO_2–11 mol%CaO solid electrolytes at 1073 K) was introduced. The wetting experiments were done in this atmosphere at the total pressure of about 0.11–0.12 MPa. After the temperature and the atmosphere had stabilized, the Al and Si segments were inserted into the bottom of the alumina tube and held for 40–90 s (depending on the testing temperature) for them to melt and alloy. The molten Al–Si alloy was then forced out through the small hole by a pressure difference created between the inside of the tube and the inside of the chamber by the gas outflow and dropped onto the α-Al_2O_3 substrate surface after about 10 s.

As soon as the drop detached from the alumina tube, a photograph was taken and defined as the drop profile at zero time. Subsequent photographs were taken at specific intervals. The captured droplet profiles were analyzed by an axisymmetric-drop-shape analysis (ADSA) program to determine the density, surface tension and contact angle simultaneously, which offers a high degree of accuracy (calculation error < ±1°) and removes the operator's subjectivity.

Results

Figure 1 shows the time variation in the contact angles for an Al–52at.%Si alloy on the R-facet α-Al_2O_3 single crystals at different temperatures. As can be seen, at $T \leq 1473$ K, the contact angles are almost constant with time, while at $T \geq 1573$ K, the contact angles show an appreciable decrease, and the decreasing magnitude increases with the temperature increase. The decrease in the contact angle is mainly attributed to the reaction between Al and Al_2O_3, as previously demonstrated in the study on the Al – Al_2O_3 system [17]. The temperature seems to have a moderate but complicated effect on the initial contact angle, as indicated in the small graph in Fig. 1, in which the minimum value appears at 1473 K.

Since the effect of temperature on the initial contact angle is not very significant, subsequent experiments were then done at temperatures about 50 K above the liquidus line (hereafter designated as T_{lq}+50 K) in the Al–Si phase diagram for the predetermined Al–Si alloy compositions, as labeled by letters from "*a*" to "*k*" in Fig. 2 and listed in detail in Table 1. The time variations in the contact angles for these alloys on the R-facet single crystals are shown in Fig. 3 and for part of the alloys on the polycrystalline α-Al_2O_3 substrates are shown in Fig. 4. Clearly, the contact angles are much smaller than 90°, except for those of the Al–25at.%Si alloy at 1073 K as a result of the Al

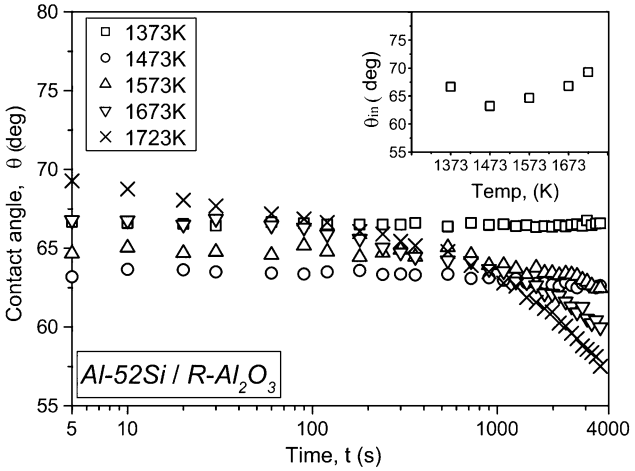

Fig. 1 Variation in the contact angles with time for an Al–52at.%Si alloy on the R-facet α-Al_2O_3 single crystals at different temperatures

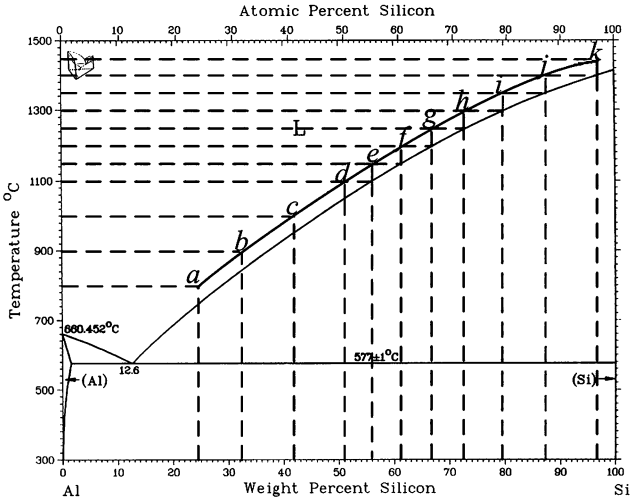

Fig. 2 Selected Al–Si alloy compositions and testing temperatures (T_{lq}+50 K) labeled by letters from "*a*" to "*f*"

surface oxidation, which is unavoidable at $T < 1173$ K under the present experimental conditions, as demonstrated in a previous study [10]. Instead, the result obtained at a higher temperature (see Fig. 5) indicates that the true contact angle of the Al–25at.%Si alloy on the R-facet alumina might be in the range of 70–80°. In this context, we can deduce that the high temperature wettability of the alumina substrates by the *clean* (inoxidized or deoxidized) Al–Si melts is quite good, even for the high Si containing alloys.

Figure 6 shows the dependence of the initial contact angle on the alloy composition for both the single crystalline and polycrystalline alumina substrates. As indicated, the contact angles for the Al–Si alloys on the polycrystalline alumina surfaces are slightly larger than those on the R-facet single crystalline surfaces. This difference could result from the influence of either the substrate surface roughness or the substrate crystallographic orientation or both. According to our previous experimental results, the wettability of α-Al_2O_3 by pure molten Al or Si is strongly dependent on the alumina surface crystallographic orientation but in different ways. In the Al/α-Al_2O_3 system, the wettability is in the order of $R(01\bar{1}2) \geq A(11\bar{2}0) > C(0001)$ [18], whereas, in the Si/α-Al_2O_3 system, it is in the order of $C(0001) > R(01\bar{1}2) \geq A(11\bar{2}0)$ [14]. The reversed sequence can reduce the effect of the alumina surface orientation on the wettability for the Al–Si/α-Al_2O_3 system. Moreover, it is interesting to note that the dependence of the contact angle on the alloy composition displays a "valley" profile with the minimum value appearing at point "*f*" for both substrates, i.e., the best wettability appears at ~62at.%Si.

Table 1 Compositions and testing temperatures for the Al–Si alloys labeled in Fig. 2

Label in the phase diagram	Temperature (K)	Si (wt.%)	Si (at.%)
a	1073	24.3	25
b	1173	32.2	33
c	1273	41.8	43
d	1373	51.0	52
e	1423	56.0	57
f	1473	61.2	62
g	1523	66.8	68
h	1573	72.5	73
i	1623	79.4	80
j	1673	87.3	88
k	1723	96.7	97

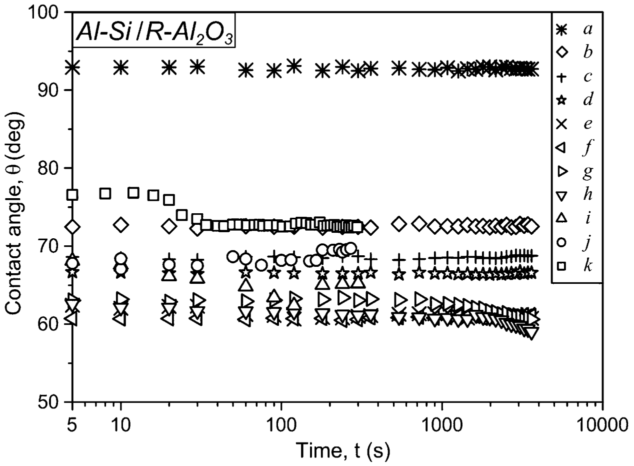

Fig. 3 Variation in the contact angles with time for various Al–Si alloys on the R-facet α-Al_2O_3 single crystals at T_{lq}+50 K

Considering that the temperature may also exert an influence on this behavior, more definitive experiments

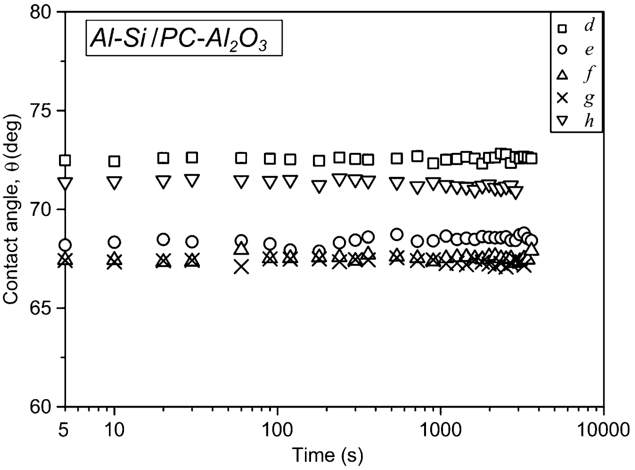

Fig. 4 Variation in the contact angles with time for part of the Al–Si alloys on the polycrystalline α-Al_2O_3 substrates at T_{lq}+50 K

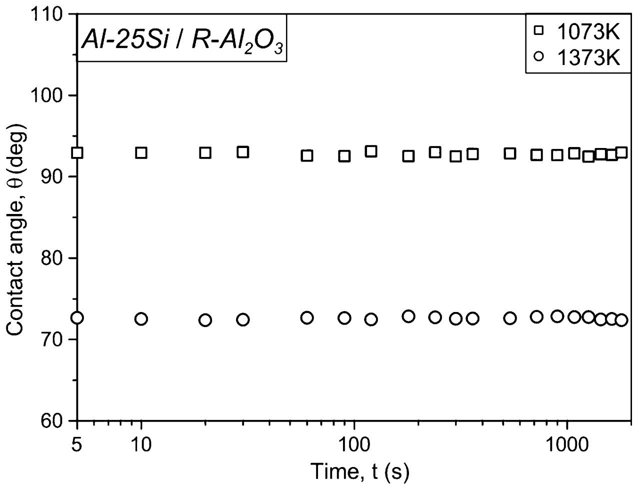

Fig. 5 Comparison of the contact angles for the Al–25at.%Si alloy on the R-facet α-Al_2O_3 single crystals at 1073 K and 1373 K

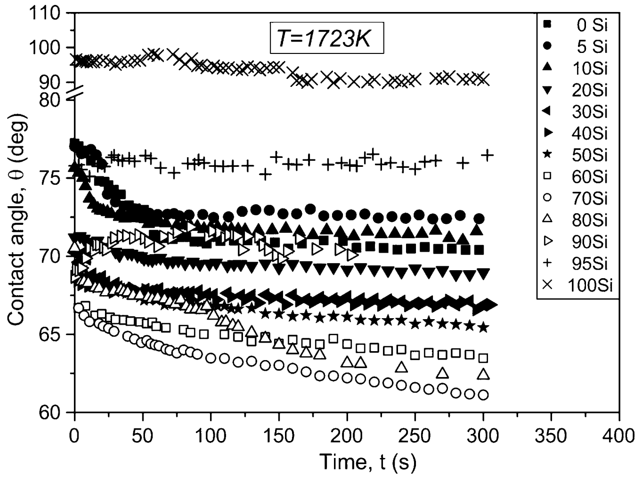

Fig. 7 Variation in the contact angles with time for the Al–Si alloys over the entire composition range on the R-facet alumina single crystals during the short time dwells at 1723 K

were done at the constant temperature of 1723 K. Figure 7 shows the time variation in the contact angles for the Al–Si alloys over the entire composition range on the R-facet alumina single crystals during the short dwell time (5 min), and Fig. 8 gives the dependence of the initial contact angles, which are characterized by the values at $t = 5$ s, on the alloy composition with some errors obtained in 2–3 runs. As indicated, the contact angles are generally much smaller than 90° except for pure Si, and a minimum interval appears in the range of 60–70at.%Si, which is similar to the foregoing results, indicating that such a behavior is an essential characteristic of the system.

Discussion

Figure 9 shows the surface tensions of the Al–Si alloys over the entire composition range at the constant temperature of 1723 K. Based on the model developed by Belton and Evan [19] and assuming that the Al–Si melts form a perfect solution, the surface tension of the alloys could be expressed by

$$\sigma = \sigma_i + \frac{kT}{a_i}\ln\frac{x_i^s}{x_i} = \sigma_i + \frac{kT}{a_i}\ln\frac{c}{1+(c-1)x_i} \qquad (2)$$

where k is the Boltzmann constant, T is the temperature, a_i is the surface area of a molecule of species i, x_i and x_i^s

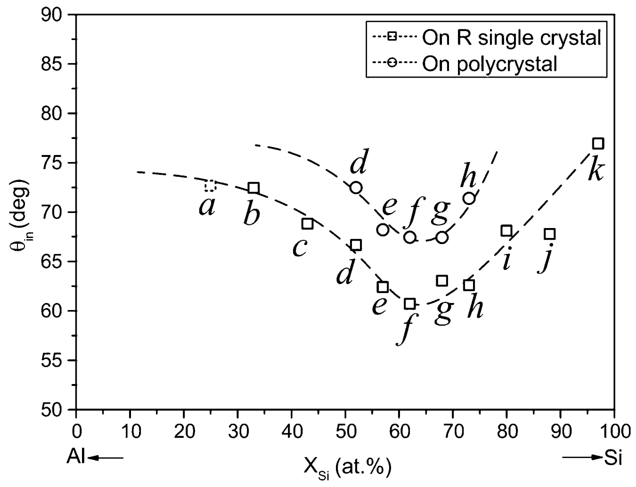

Fig. 6 Dependence of the initial contact angle on the alloy composition for the Al–Si melts on both the single crystalline and polycrystalline alumina substrates at T_{lq}+50 K except for point "a", which shows the result at 1373 K

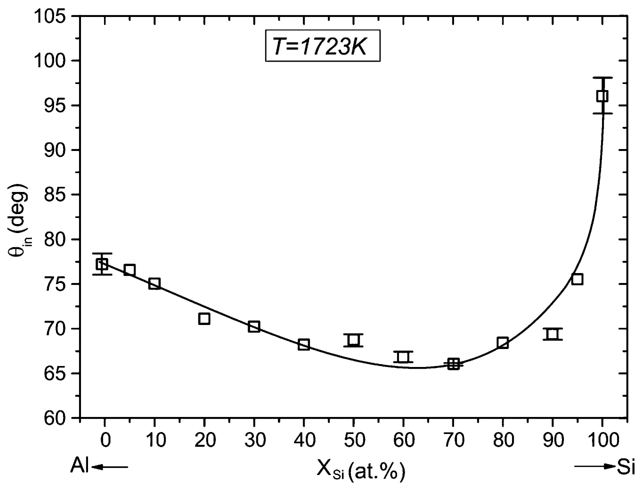

Fig. 8 Dependence of the initial contact angle on the alloy composition for the Al–Si alloys on the R-facet single crystals at 1723 K (the error bars show the errors obtained in 2–3 runs of the experiments)

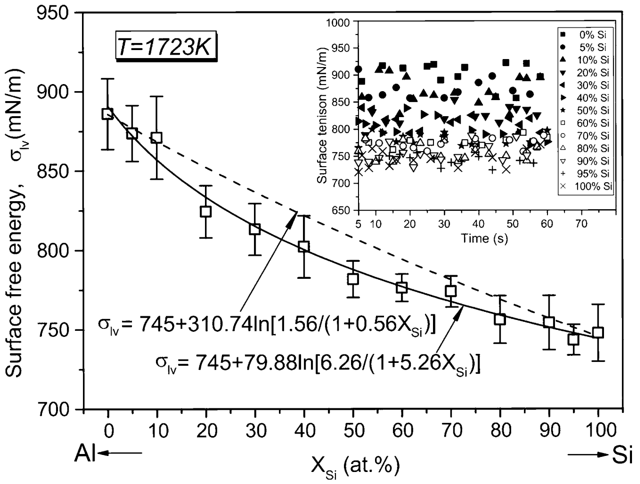

Fig. 9 Variation in the surface tension with the alloy composition at 1723 K. The given data are the average value at times between 5 and 60 s for each alloy (as indicated in the small graph) with the standard deviation results. The dot line represents the calculated result assuming the Al–Si melt being a perfect solution

are the bulk mole fraction and surface mole fraction of species *i*, respectively, and *c* is the constant. The values of a_i and *c* are given by [19, 20]

$$a_i = gN^{1/3}V_i^{2/3} \tag{3}$$

$$c = \exp[a_i(\sigma_2^0 - \sigma_1^0)/kT] \tag{4}$$

where *g* is the geometric factor (1.091 for a close-packed lattice), *N* is the Avogadro number, V_i is the molar volume of species *i*, and σ_i^0 is the surface tension of pure species *i*.

Using these equations, the surface tension of the Al–Si alloys in a perfect solution could be expressed as

$$\begin{aligned}\sigma_{\mathrm{Al-Si}} &= 745 + 310.74\ln\left(\frac{1.56}{1+0.56x_{\mathrm{Si}}}\right)\\ &= 883 - 310.74\ln(1+0.56x_{\mathrm{Si}}) \quad \mathrm{mJ\,m^{-2}},\end{aligned} \tag{5}$$

which is indicated by the dot line in Fig. 9. Obviously, the measured surface tensions deviate considerably from the calculated results, indicating that the real Al–Si solution is not perfect. Using the form of Eq. 2, the measured surface tensions could be regressed as

$$\begin{aligned}\sigma_{\mathrm{Al-Si}} &= 745 + 79.88\ln\left(\frac{6.26}{1+5.26x_{\mathrm{Si}}}\right)\\ &= 891 - 79.88\ln(1+5.26x_{\mathrm{Si}}) \quad \mathrm{mJ\,m^{-2}}.\end{aligned} \tag{6}$$

The negative deviation from the values of an ideal solution is due to the Si segregation at the liquid surface, which lowers the surface tension and thus promotes the wettability for a wetting ($\theta < 90°$) system.

On the other hand, if we assume a constant value of the alumina surface free energy, $\sigma_{\mathrm{Al_2O_3}}$, during the initial wetting stages for a given temperature, the relations among the free energies in the systems of Si–Al_2O_3 and (Al–Si)/α-Al_2O_3 based on Young's equation are

$$\begin{aligned}\sigma_{\mathrm{Al_2O_3}} &= \sigma_{\mathrm{Si-Al_2O_3}} + \sigma_{\mathrm{Si}}\cos\theta_{\mathrm{Si}}\\ &\qquad (\text{for the}\quad \mathrm{Si-Al_2O_3}\quad \text{system})\\ &= \sigma_{\mathrm{(Al-Si)-Al_2O_3}} + \sigma_{\mathrm{Al-Si}}\cos\theta_{\mathrm{Al-Si}}\\ &\qquad [\text{for the}\quad \mathrm{(Al-Si)/\alpha\text{-}Al_2O_3}\quad \text{system}]\end{aligned} \tag{7}$$

Therefore, $\sigma_{\mathrm{(Al-Si)-Al_2O_3}}$ can be expressed relative to $\sigma_{\mathrm{Si-Al_2O_3}}$ as

$$\sigma_{\mathrm{(Al-Si)-Al_2O_3}} = \sigma_{\mathrm{Si-Al_2O_3}} + \sigma_{\mathrm{Si}}\cos\theta_{\mathrm{Si}} - \sigma_{\mathrm{Al-Si}}\cos\theta_{\mathrm{Al-Si}} \tag{8}$$

Since $\sigma_{\mathrm{Al-Si}} > \sigma_{\mathrm{Si}} > 0$ (see Fig. 9) and $\theta_{\mathrm{Al-Si}} < 90 < \theta_{\mathrm{Si}}$ (see Figs. 7 and 8), we obtain the following relationship

$$\sigma_{\mathrm{(Al-Si)-Al_2O_3}} < \sigma_{\mathrm{Si-Al_2O_3}} \tag{9}$$

i.e., the addition of Al to Si reduces the solid–liquid interfacial free energy, thus promoting the wettability. Using the Gibbs adsorption isotherm equation, we have demonstrated that Al tends to segregate at the Si(–Al)/α-Al_2O_3 interface and thus acts as an effective interface tensioactive element [16].

Conclusions

The wetting behaviors of the R($01\bar{1}2$)-facet single crystalline and polycrystalline α-Al_2O_3 substrates by the Al–Si alloys over wide composition and temperature ranges were studied and the following conclusions were drawn:

(1) The wettability is good for all compositions of the Al–Si alloys, except for pure Si. The results imply that, on the one hand, the adhesion between alumina and the Al–Si alloys could be strong, and on the other hand, from the viewpoint of wetting, it is technically feasible to fabricate the (Al – Si)/α-Al_2O_3 composites, even for high Si containing alloys, by the pressureless infiltration technique if the surface oxidation of the Al–Si melts could be controlled.

(2) In the case of the clean Al–Si melts, the effect of temperature on the wettability is moderate while

that of the composition is significant. The best wettability appears when the Si content is in the range of 60–70at.%.

(3) The wetting improvement by the addition of Al to Si results mainly from the decrease in the solid–liquid interfacial free energy by the Al segregation at the interface while that by the addition of Si to Al results from the decrease in the surface tension of the liquid by the Si segregation at the surface.

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